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(54) Title: POLYESTER FOAM FOR USE IN A MODIFIED ATMOSPHERIC PACKAGE

(57) Abstract

A modified atmospheric package for containing foodstuffs without spoilage is made from a tray of a foamed thermoformable polyester and a film lid of a non-thermoformed polymer. The foamed polyester is made from repeat units from an acid component of at least 65 mole percent terephthalic acid or naphthalenedicarboxylic acid and repeat units from a glycol component of at least 65 mole percent ethylene glycol or 1,4-cyclohexanedimethanol.

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POLYESTER FOAM FOR USE IN A MODIFIED ATMOSPHERIC PACKAGE

CROSS REFERENCES TO RELATED APPLICATIONS

This application claims the benefit of United States Provisional Application Serial No. 60/078,883 filed March 20, 1998.

TECHNICAL FIELD OF THE INVENTION

This invention relates to materials used in food packaging, and more particularly to materials used in modified atmosphere packaging systems.

BACKGROUND OF THE INVENTION

In the packaging of foods and other substrates, which tend to deteriorate under normal atmospheric conditions, modified atmosphere packages (MAP(s)) are often necessary. MAP is a term applied to a range of food packaging technologies that rely on mixtures of the atmospheric gases, such as oxygen, carbon dioxide and nitrogen, in concentrations which are different from those normally found in air in order to retard deterioration processes in foods. Sometimes small amounts of other gases such as carbon monoxide, ethanol, sulfur dioxide, argon, and the like are added to maintain foods in a "fresh" state for periods of time necessary to move them through extended distribution and marketing chains. MAP is reviewed in The Wiley Encyclopedia of Packaging Technology (second Edition), John Wiley & Sons, Inc., pp 650-659 (1977), which is herein incorporated by reference.

Most MAPs are based on flexible and/or rigid monolayer or multilayer structures, which are made from plastic films or plastic and composite films, to maintain an appropriate atmosphere within the package. The most commonly used plastics include polyethylene, polypropylene, polyesters, polycarbonate, polystyrene, nylon, ethylene vinyl alcohol copolymers,

poly(vinylidene chloride) (PVDC), cellophane, rubber, and butadiene polymers. Chlorine containing polymers such as PVDC are undesirable from an environmental standpoint. Some of these polymers have also been foamed for use in MAPs. Foaming polymers reduces their densities, which makes them economically attractive. However, void spaces in foamed materials often deleteriously affect gas transmission properties to such an extent that the foamed materials are not useful for MAPs. Thus, selection of foamed materials is limited.

Furthermore, many of these polymers do not have desirable gas transmission or gas barrier properties for use in specific MAPs to maintain the desired oxygen content. For example, fresh red meat needs a good supply of oxygen to maintain an attractive red color. In other cases, oxygen must be avoided to prevent degradation of food products. Commercial analyzers test the oxygen content within the headspace of sealed packages. With these instruments, the headspace is tested by piercing the lid with a syringe, which sends the headspace gas to a detector. An example of this type of instrument is the PBI-Dansensor IEA LV HeadSpace Oxygen Analyzer utilized below.

To obtain the necessary barrier requirements for some food packages, multi-layer high barrier films are applied to base film or rigid materials providing low gas permeability rates. These films are typically applied either by post or in-line process lamination or possibly in a co-extrusion process. These high barrier films are typically specialized films and are relatively high in costs to the package manufacturer. U.S. Patent Nos. 4,840,271 and 5,025,611 describe packages derived from multi-layered structures containing poly(vinyl chloride) laminated with other polymers such as polyethylene, ethylene/vinyl acetate copolymers, and poly(vinylidene chloride) and an apparatus for packaging perishable goods in such packages. Another example of a multi-layered structure is that disclosed in WO 95/15257. This reference discloses a food packaging

material having a foamed thermoplastic core layer and at least one non-foamed thermoplastic barrier layer.

Current MAPs are also limited as to their end use temperature capabilities. For example, laminated foamed polystyrene is limited to about 100°C, is unsuitable for either microwave or conventional oven uses and requires an expensive barrier layer. Both talc filled and foamed polypropylene have an end use temperature of about 130°C, limiting their use to only certain microwave applications. Polypropylene is also unsuitable for conventional oven uses and requires an expensive barrier layer to function in even the most fundamental MAP applications.

Thus, there exists a need in the art to have lightweight trays for use in MAP applications that are useable in both conventional and microwave ovens (known as dual-ovenability) and have the desired barrier properties. Accordingly, it is to the provision of such trays that the present invention is primarily directed.

BRIEF SUMMARY OF THE INVENTION

A lightweight modified atmospheric package comprises a tray of a foamed thermoformable polyester and a lid. The polyester comprises repeat units from an acid component of at least 65 mole percent terephthalic acid or naphthalenedicarboxylic acid and repeat units from a glycol component of at least 65 mole percent ethylene glycol or 1,4-cyclohexanedimethanol. The modified atmospheric package preferably maintains a gas level with maximum loss of the gas at about 10 percent after 20 days at ambient temperature.

The tray is preferably a monolayer of the foamed thermoformable polyester having a density of from about 0.1 g/cc to about 1.2 g/cc.

DETAILED DESCRIPTION OF THE INVENTION

A material for use in a modified atmospheric package (MAP) is made of certain foamed polyester and has unexpectedly been found to provide a lightweight tray with desired barrier properties and may also be utilized in dual-ovenable applications. Previously, the foaming of a poly(ethylene terephthalate) (PET) was expected to deleteriously affect its gas transmission properties to such an extent that it would not be useful as a tray for MAP applications.

The MAP of the present invention is used to contain foodstuffs without spoilage and is made of a tray of a foamed thermoformable polyester and a lid. The MAP preferably maintains a gas level with maximum loss of gas at about 10 percent after 20 days at ambient temperatures of about 73°F (22.5°C).

The polyesters for use as the tray comprise repeat units of an acid component of at least 65 mole percent terephthalic acid or naphthalene-dicarboxylic acid and repeat units of a glycol component of at least 65 mole percent ethylene glycol or 1,4-cyclohexanedimethanol. Suitable polymers will have inherent viscosity (I.V.) values in the range of about 0.5 to about 1.5 dL/g with those having I.V. values of 0.6 to 1.0 dL/g being preferred. The polyesters are readily prepared by melt phase and/or solid phase polycondensation techniques well known in the art.

Homopolymers such as PET, PEN, poly(1,4-cyclohexylene-dimethylene terephthalate) (PCT), and poly(1,4-cyclohexylenedimethylene naphthalenedicarboxylate) (PCN) are readily usable, as well as copolyesters containing up to about 35 mole percent modifying dibasic acids or glycols. Suitable modifying dibasic acids include those containing about 4 to about 40 carbon atoms and include terephthalic, naphthalene-dicarboxylic, succinic, glutaric, azelaic, adipic, suberic, sebacic, isophthalic, sulfoisophthalic, 1,4-cyclohexanedicarboxylic acids and the like. Any of the naphthalenedicarboxylic acid isomers or mixtures of isomers may be used

but the 1,4-, 1,5-, 2,6-, and 2,7- isomers are preferred. The cis-, trans-, or cis/trans mixtures of 1,4-cyclohexanedicarboxylic acid may be used. Useful modifying glycols include ethylene glycol, diethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, 1,4-cyclohexanedimethanol and the like. Cis-, trans- or cis/trans mixtures of 1,4-cyclohexanedimethanol may be used.

The foamed polyesters of the present invention will generally have densities of about 0.1g/cc to about 1.2 g/cc, with densities of about 0.3 g/cc to about 0.9 g/cc. preferred. The foamed polyesters are typically in sheet form having a thickness of about 5 mils (0.125 mm) to 90 mils (2.25 mm), preferably about 10 mils (0.25 mm) to 40 mils (1 mm). Optionally, a non-foamed cap layer made from the same polyester or another polymer may be applied to the foamed polyester to provide a smooth surface appearance. The cap layer has a thickness of about 0.5 mils (0.0125 mm) to 20 mils (0.5 mm), preferably 1.0 mils (0.025 mm) to 10 mils (0.25 mm).

The polyesters of the present invention are readily foamed by any of the techniques described in U.S. Patent Nos. 5,399,595, 5,482,977, 5,519,066, and 5,696,176. A preferred foaming process is described in U.S. 5,654,347. All the above patents are herein incorporated by reference.

For the foam processes using chemical blowing agents, PET copolyesters that are more hydrolytically stable are preferred. Such copolyesters contain repeat units from terephthalic acid, about 60 to 80 mole percent ethylene glycol and 40 to 20 mole percent 1,4-cyclohexanedimethanol.

For the foam processes using inert gases as blowing agents, PET polymers with I.V. values of at least about 0.85 dL/g are used in order to provide sufficient melt strength for good foaming characteristics. For PET polymers with I.V. values less than 0.85 dL/g, branching agents at up to about 2 mole percent may be used to increase the melt viscosity and melt

strength of the PET polymer during the foaming operation. The increase in melt viscosity and melt strength enhances the foaming characteristics of the polyesters. Suitable branching agents include polyfunctional acids, polyols, or hydroxy acids containing from three to about six functional groups. Some useful ones include trimellitic acid, trimellitic anhydride, pyromellitic dianhydride, trimethylolpropane, pentaerythritol, glycerine, malic acid, citric acid, tartaric acid, 3-hydroxyglutaric acid, 4-(β-hydroxyethyl) phthalic acid and the like. Other suitable branching agents are disclosed in U.S. Patent No. 5,654,347.

In order to seal the MAP, a lid is placed atop the tray. The lid is preferably a film having a thickness of about 0.5 mils (0.0125 mm) to 20 mils (0.5 mm). The film is typically made of a polymer that has high barrier properties such as PET or poly(ethylene naphthalenedicarboxylate) (PEN).

Packages made from the foams of the present invention are useful for a wide range of foods including cooked or raw red meat, fish or chicken; cooked or chilled food; prepared meals; vegetables; fruits; nuts and the like. In many cases, the packages will be stored for use for only 1 to about 10 days. However, in some cases, storage may be for up to 1 year. The type of atmosphere in the packages will vary depending on the food product being stored. However, the gases used may include oxygen, nitrogen, carbon monoxide, carbon dioxide, ethanol, sulfur dioxide, argon and the like or mixtures of these gases.

The packaging materials of this invention are based on commercially available polyesters which are economical to use and recyclable. They do not contain chlorine and do not require the use of high barrier laminated materials which are expensive.

Inherent viscosity (I.V.) as used herein refers to viscosity determinations made at 25°C using 0.25 gram of polymer per 100 mL of a solvent composed of 60 weight percent phenol and 40 weight percent tetrachloroethane.

This invention can be further illustrated by the following examples of preferred embodiments thereof, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated.

Example 1 - PET Foamed Tray

The oxygen permeability of a mono-layered amorphous PET foamed sheet was measured to be 77.6 cc•mil/100 in^2 •24 hr•atm at 23°C (156.0 amol/m^2•Pa) and 50% relative humidity. The density of the sheet was 0.65 grams/cubic centimeter (g/cc) and the thickness was 0.024 inches (0.60 mm). Obvious to those skilled in the art, a package has an oxygen permeability value equal to the sheet from which it is made assuming equal material thickness in the package. Thus, a package comprising a tray made from this sheet has an area of 61.5 in^2 (0.04 sq-meter) with a measured volume of 714.2 cc. The tray is flushed with 1 atm (101.33 kPa) of a mixture of atmospheric gases containing 70% oxygen and sealed with a barrier lid such as oriented PET film. The package initially has a volume of oxygen of 500 cc. After 10 days the volume of oxygen is 490 cc, which equates to 68.5% oxygen remaining in the package. After 20 days, 67.2% of oxygen remains in the package. The oxygen retention of the package is improved when stored under refrigerated conditions. The oxygen retention is also improved when the package has been manufactured in such a manner as to introduce crystallinity.

Example 2 - Three Layer PET Foamed Tray

A sheet was made having a three-layered structure with a total overall thickness of 0.024 inches (0.6 mm). The sheet had a core layer of the foamed PET polyester of Example 1 at a thickness of 0.02 inches (0.50 mm) and two outer layers of solid PET polyester at a thickness of 0.002

inches (0.05 mm). The sheet had an oxygen permeability of 49.3 cc•mil/100 in^2 •24 hr•atm at 23°C C (99.1 amol/m^2•Pa) and 50% relative humidity. The density of the sheet was 0.60 g/cc. A package comprising a tray made from this sheet has a measured volume of 714 cc. The tray is flushed with 1 atm (101.33 kPa) of a mixture of atmospheric gases containing 70% oxygen and sealed with an oriented PET film of 1.0 mil (0.025 mm). After 10 days, the oxygen level of the package is 69%, and after 20 days the oxygen level is 68%. The oxygen retention of the package is improved when stored under refrigerated conditions. The oxygen retention is also improved when the package has been manufactured in such a manner as to introduce crystallinity.

Example 3 - PET Foamed Tray Containing Red Meat

The tray made of the sheet of Example 1 is filled with red meat to the 50% volume level and flushed with 1 atm (101.33 kPa) of a mixture of atmospheric gases containing 70% oxygen. The tray is sealed with an oriented PET polyester lidding film of 1.0 mil (0.025 mm) to make a modified atmospheric package for storing red meat. The package is stored under ambient conditions. After 10 days the oxygen level of the package is 67%. After 20 days the oxygen level is 64%. The red color of the meat is retained. The oxygen retention of the package is improved when stored under refrigerated conditions. The oxygen retention is also improved when the package has been manufactured in such a manner as to introduce crystallinity.

Example 4 - Three layer PET Foamed Tray Containing Red Meat

A tray made of the sheet of Example 2 is filled with red meat to the 50% volume level and flushed with 1 atm (101.33 kPa) of a mixture of atmospheric gases containing 70% oxygen. The tray is sealed with an oriented PET polyester lidding film of 1.0 mil (0.025 mm) to make a

modified atmospheric package for storing red meat. The package is stored under ambient conditions. After 10 days the oxygen level of the package is 68%. After 20 days the oxygen level is 66%. The red color of the meat is retained. The oxygen retention of the package is improved when stored under refrigerated conditions. The oxygen retention is also improved when the package has been manufactured in such a manner as to introduce crystallinity.

Similarly good results are achieved when the lidding film is Dupont Mylar BA1 high barrier film, which is a PVDC copolymer coated PET.

Example 5 - PET Copolyester Foamed Tray

A three-layered sheet is made having a core layer of a foamed PET copolyester containing 100 mole % terephthalic acid, 69 mole % ethylene glycol and 31 mole % 1,4-cyclohexanedimethanol (I.V. 0.76 dL/g) and two solid PET outer layers. The core layer has a thickness of 0.02 inches (0.50 mm), and the outer layers have a thickness of 0.002 inches (0.05 mm). A tray is made from the sheet. The tray has a density of 0.64 g/cc and a volume of 714 cc. The tray is flushed with 1 atm (101.33 kPa) of a mixture of atmospheric gases containing 70% oxygen and sealed with an oriented PET lidding film of 1.0 mil (0.025 mm) to form a package. The package is stored at ambient conditions for 10 days and the oxygen content of the gaseous mixture in the package is 69%. When red meat is stored in this type of package for 10 days at 36°F (2.2°C) in the presence of 70% oxygen, the red color of the meat is retained. The oxygen retention of the package is improved when stored under refrigerated conditions. The oxygen retention is also improved when the package has been manufactured in such a manner as to introduce crystallinity to the outside rigid PET layers.

Example 6 - PEN Foamed Tray

A package is prepared using the general procedure of Example 1. The package comprises a tray made using foamed PEN polyester sheet (I.V. 0.72 dL/g) having a density of 0.65 g/cc. After flushing the tray with a gas mixture containing 70% oxygen and sealing with an oriented PEN polyester lidding film (1 mil), a package is produced and stored at 36°F (2.2°C) for 10 days. After this time the oxygen content of the package is 69%. The oxygen retention of the package is improved when stored under refrigerated conditions. The oxygen retention is also improved when the package has been manufactured in such a manner as to introduce crystallinity to the outside rigid PEN layers.

Similarly good results are achieved with a foamed sheet made from PEN copolyester containing 90 mole % naphthalenedicarboxylic acid, 10 mole % terephthalic acid, and 100 mole % ethylene glycol (I.V. 0.75 dl/g).

Example 7 - PET Foamed Tray Containing Chicken Breasts

Trays are made according to the procedure of Example 2 and using the materials of Example 2. The trays are filled with fresh chicken breasts and flushed with a mixture of 30% carbon dioxide and 70% nitrogen. The trays are sealed with an oriented PET polyester lidding film forming a package. The package is then stored at 36°F (2.2°C) for 10 days. The chicken parts retain a good appearance.

Similarly good results are achieved when the foamed polyester was derived from PET copolyester containing 95 mole % terephthalic acid, 5 mole % isophthalic acid, and 100 mole % ethylene glycol.

Similarly good results are also achieved when pork chops are stored in the package in the presence of 50% carbon dioxide and 50% nitrogen for 7 days at 36°F (2.2°C).

By the present invention, lightweight trays made of foamed thermoformable polyester are now available for use in MAP applications. The trays are suitable for use in both conventional and microwave ovens. The trays in conjunction with a lid provide a modified atmospheric package that has the desired barrier properties to adequately seal food for long periods of time.

CLAIMS

We claim:

1. A modified atmospheric package comprising:
   a) a tray comprising a foamed thermoformable polyester comprising repeat units from an acid component of at least 65 mole percent terephthalic acid or naphthalenedicarboxylic acid and repeat units from a glycol component of at least 65 mole percent ethylene glycol or 1,4-cyclohexanedimethanol.
   b) a lid.

2. The modified atmospheric package of claim 1 maintaining a gas level with maximum loss of the gas at about 10 percent after 20 days at ambient temperature.

3. The modified atmospheric package of claim 1 wherein the tray consists essentially of the foamed thermoformable polyester.

4. The modified atmospheric package of claim 1 wherein the tray consists of the foamed thermoformable polyester.

5. The modified atmospheric package of claim 1 wherein the tray is a monolayer of the foamed thermoformable polyester.

6. The modified atmospheric package of claim 1 wherein the foamed thermoformable polyester has a density of from about 0.1 g/cc to about 1.2 g/cc.

7. The modified atmospheric package of claim 1 wherein the foamed thermoformable polyester has a density of from about 0.3 g/cc to about 0.9 g/cc.

8. The modified atmospheric package of claim 1 wherein the foamed thermoformable polyester has a thickness of from about 5 mils (0.125 mm) to 90 mils (2.25 mm).

9. The modified atmospheric package of claim 1 wherein the foamed thermoformable polyester has a thickness of from about 10 mils (0.25 mm) to 40 mils (1 mm).

10. The modified atmospheric package of claim 1 wherein the polyester is a homopolymer selected from poly(ethylene terephthalate), poly(ethylene naphthalenedicarboxylate), poly(1,4-cyclohexylenedimethylene terephthalate) and poly(1,4-cyclohexylenedimethylene naphthalenedicarboxylate).

11. The modified atmospheric package of claim 1 wherein the acid component further comprises dibasic acids containing about 4 to about 40 carbon atoms.

12. The modified atmospheric package of claim 1 wherein the acid component further comprises terephthalic acid, naphthalenedicarboxylic acid, isophthalic acid, sulfoisophthalic acid, 1,4-cyclohexanedicarboxylic acid, succinic acid, glutaric acid, azelaic acid, adipic acid, suberic acid, sebacic acid or mixtures thereof.

13. The modified atmospheric package of claim 1 wherein the glycol component further comprises ethylene glycol, diethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, 1,4-cyclohexanedimethanol or mixtures thereof.

14. The modified atmospheric package of claim 1 wherein the lid is a film having a thickness of about 0.5 mils (0.0125 mm) to 20 mils (0.5 mm).

15. The modified atmospheric package of claim 1 wherein the lid comprises a polymer having high barrier properties.

16. The modified atmospheric package of claim 1 wherein the lid comprises a polymer selected from poly(ethylene terephthalate) and poly(ethylene naphthalenedicarboxylate).

17. The modified atmospheric package of claim 1 containing cooked or raw red meat, fish, or chicken.

18. The modified atmospheric package of claim 1 containing gases selected from oxygen, nitrogen, carbon monoxide, carbon dioxide, ethanol, sulfur dioxide, argon or mixtures thereof.

19. The modified atmospheric package of claim 1 wherein the tray further comprises a non-foamed cap layer on a surface of the foamed thermoformable polyester.

20. The modified atmospheric package of claim 19 wherein the non-foamed cap layer comprises a polyester.

21. The modified atmospheric package of claim 19 wherein the non-foamed cap layer has a thickness of about 0.5 mils (0.0125 mm) to 20 mils (0.5 mm).

22. The modified atmospheric package of claim 19 wherein the non-foamed cap layer has a thickness of about 1.0 mils (0.025 mm) to 10 mils (0.25 mm).

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/04761

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B65D81/20 C08L67/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B65D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 97 15627 A (BORDEN GLOBAL PACKAGING UK LTD) 1 May 1997 (1997-05-01) abstract; claim 10; examples 4,5 page 7, line 35 - page 8, line 29 ---	1,3-10, 14,15, 17-22
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Y	WO 95 15257 A (PLM AB) 8 June 1995 (1995-06-08) cited in the application page 1, line 1 - line 19; claims 1-7 --- -/--	1,3-10, 14,15, 17-22

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

International Application No
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